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ABSTRACT. The formation of molybdenum nitrides was investigated at temperatures up to 1200°C in flowing ammonia with various flow rates and reaction times. The products were characterised by XRD, chemical analysis, metallography and EPMA. The phases γ-MoN_{1-x} and δ-MoN formed at temperatures above 600°C only at high flow rates of about 20l/h. If the flow decreases even powders did not show the δ-MoN phase. β-Mo_2N was observed by XRD in both, powder samples and compact samples. While a distinct and dense γ-MoN_{1-x} layer formed, the layer of δ-MoN was too thin to be detected by metallography of the wedge-type samples and could only be observed by XRD of the surface. Microhardness of a γ-MoN_{1-x} diffusion layer revealed at 1000°C was measured as a function of composition. The homogeneity range of γ-MoN_{1-x} at around 900-1000°C was determined by EPMA. The diffusivity of nitrogen in γ-MoN_{1-x} at 1000°C was calculated.

INTRODUCTION

Molybdenum nitrides are interesting as materials with high hardness and superconductors with critical temperatures between 5 and 14.9K [1]. Details on the formation temperature, phase relationships and properties of molybdenum nitrides are still incompletely known. They have high nitrogen equilibrium pressures so that nitridation has to be performed in flowing ammonia unless high-pressure equipment is used. This can be made by using molybdenum compounds such as sulphides [2] or chlorides [3]. However, in order to study the in-diffusion of nitrogen into Mo metal the most straightforward technique is to use Mo sheet and powder as a starting material.

EXPERIMENTAL

The nitridation reactions were carried out in a horizontal open-flow system with Mo (powder or sheet and/or wedge) in a ceramic boat under the flow of NH_3 (Fig. 1). The NH_3 was passed through a separate tube into the reaction zone to prevent decomposition [3]. The nitriding conditions for the sheets and wedges are presented in Table 1. After the nitridation, a part of the samples were cooled down to room temperature under nitrogen atmosphere the other in NH_3.

Table 1
Conditions for the nitridation experiments

temperature [°C]	NH_3 -flow [l/h]	reaction time [h]
1200	10	40
1050	7	20
1000	20	15 and 37
1000	40	15
1000	10	40
1000	7	20
900	20	24, 30, 44 and 72
850	7	20
781	8	40
600	20	62
300	20	47

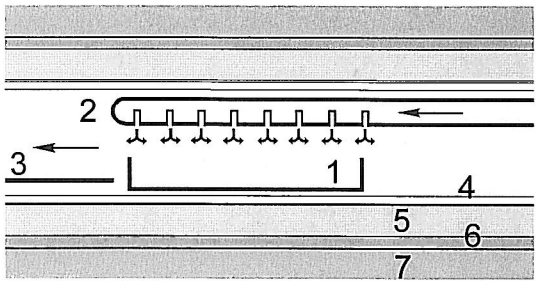

Fig. 1
Scheme of the nitridation furnace
1 ceramic boat; 2 NH_3-supply; 3 thermo-couple; 4 SiO_2 tube; 5 tube with filament winding; 6 ceramic tube; 7 insulation-wool

The nitrided samples were subjected to metallography, XRD, chemical analysis and EPMA. To detect thin layers and/or gradients in the microstructure at the outermost surface of the samples glancing angle XRD (GAXRD) was used to obtain depth-resolved information. Thereby the dependence of the penetration depth on the angle of incidence of the incoming beam is used. The microhardness of the γ-MoN_{1-x} phase was measured as a function of composition from a diffusion layer obtained at 1000°C at a load of 5N.

RESULTS

By XRD analysis of the powder samples different molybdenum-nitride phases were found. Nitriding conditions, detected phases by XRD and results of the chemical analysis are given in Table 2. These experiments show that nitrogen diffusivity is such slow that even the powder particles on the order of ca. 10µm in diameter are not completely nitrided. The flow rate is also important at these relatively high temperatures because of ammonia decomposition. Thus, the higher the flow rate the higher the amount of undecomposed NH_3 reaching the sample and the higher

Table 2
Nitriding conditions and phase analysis of molybdenum nitride powders

reaction temperature [°C]	NH_3 flow rate [l/h]	reaction time [h]	detected phases (XRD)	chemical analysis [wt%] N	O
1000	~5	20	Mo, γ-MoN_{1-x}, β-Mo_2N	4.903 4.941	0.3861 0.3108
1000	~7	20	Mo, γ-MoN_{1-x}, β-Mo_2N	5.828 5.869 5.872	0.3046 0.3466 0.2278
1100	~7	20	Mo, γ-MoN_{1-x}, β-Mo_2N	5.102 5.231	0.2341 0.3409 0.2300

the nitrogen content of the product. If the temperature is increased to 1100°C the nitrogen content lowers (at the same experimental conditions) due to the higher nitrogen equilibrium pressure of the solid phase.
A typical microstructure of a molybdenum-nitrogen diffusion wedge is presented in Fig. 2. It shows a compact and well-adhering γ-MoN_{1-x} layer at the outermost part and molybdenum in the core.

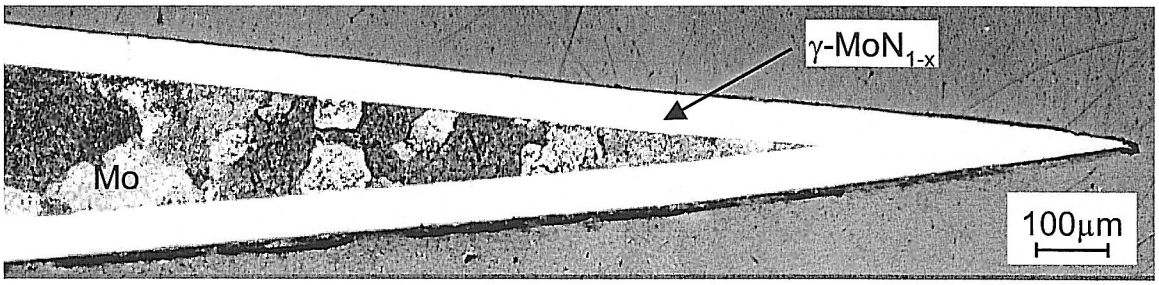

Fig. 2
Microstructure of a diffusion wedge, (1000°C; 20l/h NH_3; 15h)

Perpendicular across the γ-MoN_{1-x} layer there were few cracks which indicates stress between the γ-MoN_{1-x} layer and the molybdenum core.
By XRD also δ-MoN was found in most samples but these layers were too thin to be prepared and observed by metallography and therefore they are not visible in the optical microscope. In Fig. 3 two GAXRD patterns measured with different angles of incidence (which means different penetration depths) of a sample, showing δ-MoN at the outermost surface, and γ-MoN_{1-x} below is presented. It can be seen that the peaks belonging to the γ-MoN_{1-x} phase are larger in the pattern which is measured using an angle of incidence of 10° which means a greater penetration depth.

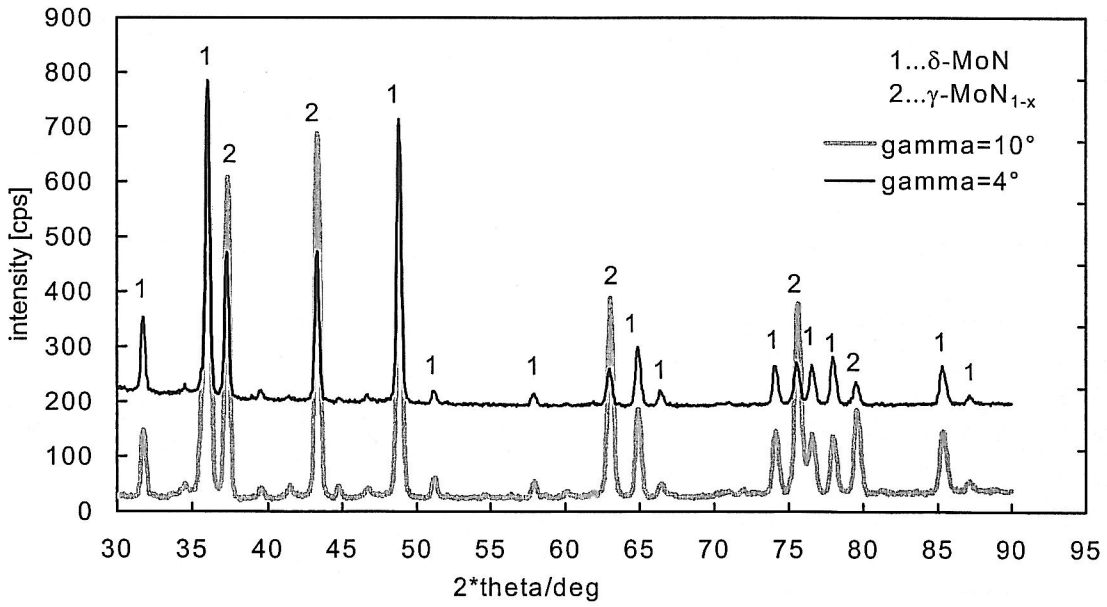

Fig. 3
GAXRD pattern of a nitrided Mo sheet; (900°C; 20l/h NH_3; 72h)

In one sheet sample an about 1µm thick β-Mo_2N layer was observed at the outermost surface (see Fig. 4). Below this layer an Mo layer was found which originally consisted of γ-MoN_{1-x}. The third layer indeed consisted of γ-MoN_{1-x}. Such a result was obtained if N_2 was used upon cooling.

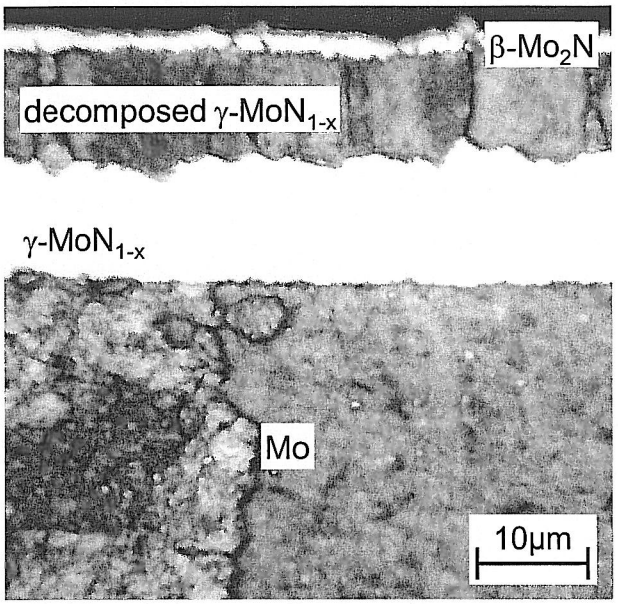

Fig. 4
Microstructure of the near surface area of a Mo-N diffusion couple; 1200°C, 10l/hNH$_3$, 40h

Obviously, nitrogen diffuses out of the sample because N_2 has a lower nitriding potential than NH_3. The reason why β-Mo_2N is formed upon this out-diffusion process can be explained by the lower nitrogen equilibrium pressure of this phase which is already achieved by the nitrogen atmosphere. To investigate the homogeneity range of the γ-MoN_{1-x} phase EPMA scans were performed. These measurements were done for two different temperatures (900°C and 1000°C). Fig. 6a presents an EPMA-scan along the nitrogen-diffusion path. From these scans the nitrogen concentration of the inner phase boundary was obtained. The nitrogen concentration of the nitrogen richer phase boundary was measured from scans along the symmetry plane of the wedge-type samples because the tip provides better analysis conditions as compared to the edge of the sample (see Fig. 6b). The results are presented in Table 3.

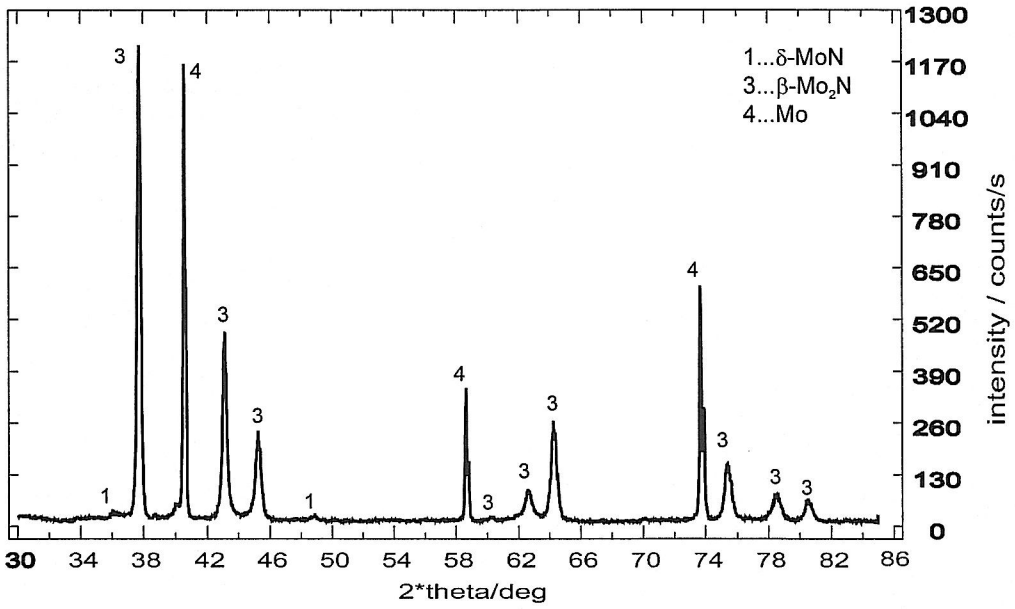

Fig. 5
XRD pattern of a sample which shows β-Mo_2N at the outermost surface (see also Fig. 4)

Table 3
Summary of the EPMA results for the system Mo-N

temperature	homogeneity range	
[°C]	concentration [at%N]	concentration [at%N]
900	28.98	38.09
1000	28.53	38.21

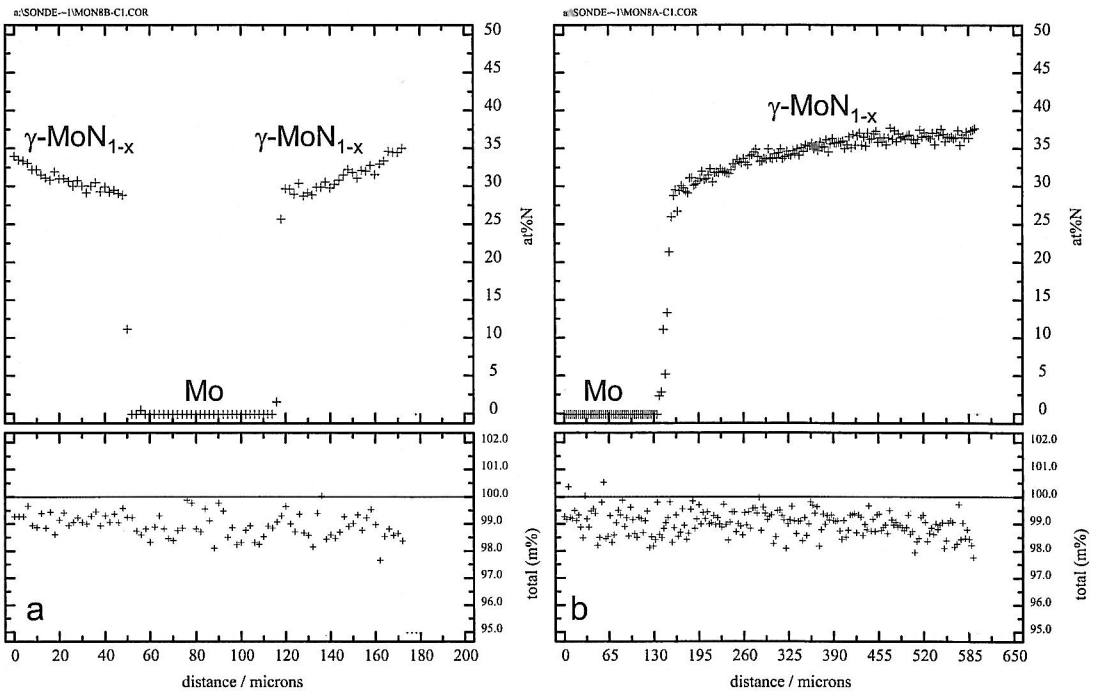

Fig.6
EPMA scans of Mo and N; a: scan along the diffusion path of N, b: scan along the symmetry plane of the wedge-type sample

Also diffusion coefficients were calculated for these two temperatures. The homogeneity ranges and the calculated coefficients are shown in Table 4.

Table 4
Homogeneity ranges and diffusion coefficients for 900°C and 1000°C

temperature	**c^+ Mo**	**c^- c^+ γ-MoN_{1-x}**		**D_α**	**D_γ**
[°C]	[molN/cm^3]	[molN/cm^3]		[cm^2/s]	[cm^2/s]
1000	0.001	0.0373	0.0572	average	average
1000	0.001	0.0369	0.0572	$1.3.10^{-9}$	$2.14.10^{-11}$
900	0.001	0.0378	0.0569	average	average
900	0.001	0.0378	0.0569	$1.2\ (\pm1).10^{-9}$	$7\ (+1,-2).10^{-11}$

The microhardness of a γ-MoN_{1-x} diffusion layer obtained at 1000°C was measured as a function of the nitrogen content and compared with data from the literature [1] (see Fig. 7). It was found that there is an increase of the microhardness with increasing of the nitrogen content. The microhardness H_v is 18.3GPa at 29.5at%N and 21.4GPa at 35.5at%N.

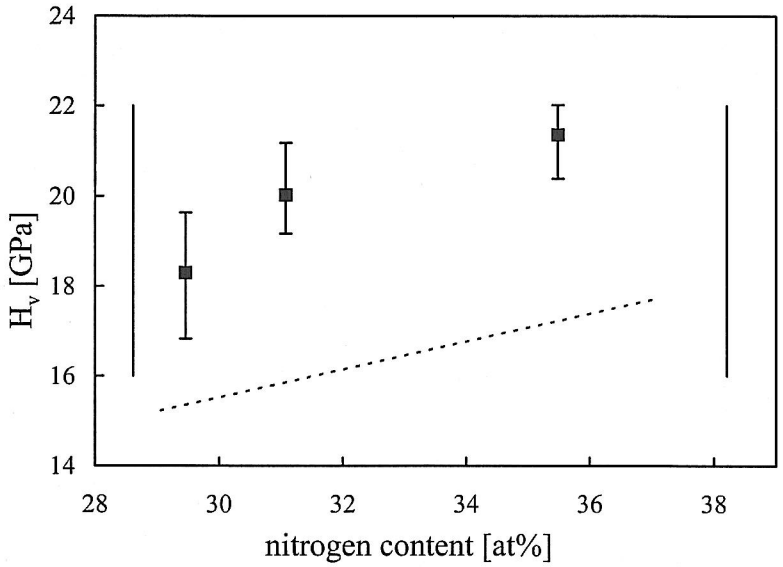

Fig. 7
Microhardness of the γ-MoN_{1-x} layer grown at 1000°C as a function of the nitrogen content; vertical lines: homogeneity range of γ-MoN_{1-x}; dash-lined line: data of [1]

CONCLUSIONS

The in-diffusion of nitrogen into molybdenum sheet and powder via flowing ammonia as nitriding agent was investigated for various temperatures. In sheet samples a distinct and dense γ-MoN_{1-x} layer formed above 600°C. δ-MoN also formed in both, powder and sheet samples, but it was too thin to be detected by metallography. Faint traces of β-Mo_2N were observed by XRD in powder samples. γ-MoN_{1-x} can transform into β-Mo_2N and/or decompose upon cooling. This phenomena has to be studied in more detail (see also [4]).
The homogeneity range of γ-MoN_{1-x} at around 900-1000°C was determinated to be 28.5-38.2at%N. The diffusivity of nitrogen in γ-MoN_{1-x} is about 2.10^{-11} cm^2/s at 1000°C.

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